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垂直定向二维纳米材料的合成及其在电化学储能和转化中的应用研究

Synthesis of Vertically Oriented Two Dimensional Nanomaterials and Their Applications in Electrochemical Energy Storage and Conversion

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Synthesis of Vertically Oriented Two Dimensional Nanomaterials and Their Applications in Electrochemical Energy Storage and Conversion

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摘要

能源危机和环境污染问题限制了经济的可持续发展，因此开发高效、环境友好的电化学能源储能和转化技术迫在眉睫。随着石墨烯的快速发展，二维纳米材料因其独特的物理化学性质、高的比表面积和二维空间的电子限域作用引起了研究者们的极大兴趣。然而二维纳米材料层间的堆叠或团聚特性不利于其表面的有效利用，特别是在应用于电化学相关领域时，不利于电子和离子的快速传输。如何提升二维纳米材料的传质和传导，是其在电化学应用中亟待解决的瓶颈问题。因此，本论文围绕着二维纳米材料的控制制备和基于二维纳米材料垂直定向组装的多级结构构造展开研究，主要研究内容和结果如下：

第一章，简要介绍了二维纳米材料在电化学储能、电催化以及吸附等领域中的结构优势和主要研究方向。总结了目前关于二维纳米材料超薄片制备技术及其垂直定向结构组装的研究现状，最后阐述了本论文的选题依据和研究内容。

第二章，通过研究 MgO 微米棒的水解过程，成功实现了 $Mg(OH)_2$ 纳米片的垂直定向组装。该方法为二维碳纳米材料的垂直结构设计提供了新的途径。

第三章，以垂直定向的 $Mg(OH)_2$ 为模板，多巴胺作为碳源，成功实现了超薄碳纳米片的垂直定向组装，解决了二维超薄碳材料的堆叠问题。系统研究有机前驱体包覆量和热处理温度对材料孔结构的影响。通过对超薄碳纳米片的表面造孔和垂直定向组装，提升了其比容量和倍率性能。该结构材料作为锂离子电池负极材料的可逆比容量高达 1150 mAh g^{-1}，是石墨的 3.1 倍，在电流密度 10 A g^{-1} 时稳定的可逆容量为 246 mAh g^{-1}。

第四章，以 $Mg(OH)_2$ 为模板，结合化学气相沉积的方法，成功制备出垂直定向多孔类石墨烯纳米片。利用该材料的多级结构优势，实现了 Li-S 电池中硫正极的高负载（78.9 wt%和 88.8 wt%），并表现出优异的比容量和体积能量密度。通过与二维多孔碳片和一维多孔碳棒对比研究表明，垂直定向多孔类石墨烯纳米片由于具有超高的比表面积和孔体积以及开放的三维导电框架，在高硫负载的锂硫电池中表现出优异的倍率性能。

第五章，以 MgO 为反应物，发展了一种在室温下宏量制备超薄α-$Ni(OH)_2$ 纳米片的绿色方法。通过对生长机制的深入了解，该方法可推广至多种单金属和

双金属氢氧化物及其衍生物的制备。由于具有高的比表面积，所制备的超薄 α-$Ni(OH)_2$ 纳米片分别在重金属吸附领域和超级电容器领域表现出优异的性能。

第六章，基于 MgO 法在室温下实现了二维过渡金属氢氧化物在基底上的垂直定向生长，解决了二维过渡金属氢氧化物堆叠和导电性差的问题。与传统的水热法和电沉积方法相比，MgO 辅助方法不受基底尺寸、形状和种类的限制。通过在三维泡沫镍表面生长 $Ni(OH)_2$ 并经过低温硫化过程得到垂直定向的硫化物纳米片，通过调节 Ni/Fe 元素组成获得了垂直定向的双金属氢氧化物纳米片，并分别研究了其电催化析氢和析氧性能。基于优异的催化性能，将制备的两类催化剂体系作为电催化分解水的阴极和阳极，在 1 M 的 KOH 电解液中，在电流密度为 10 mA cm^{-2} 下，水分解电压仅为 1.55 V。

关键字：二维纳米材料；垂直定向结构；储能；电解水；氧化镁

Abstract

Since energy crisis and environmental pollution have restricted the sustainable development of economy, there is an urgent need to develop the efficient and environmentally friendly electrochemical technologies for energy storage and conversion. With the rapid progress of graphene, two dimensional (2D) nanomaterials have become a hot research field due to their unique physical and chemical properties, such as high specific surface area and the dimensionality effect and modulation. However, the inevitable re-stacking or aggregation of 2D nanomaterials has greatly impeded the full utilization of their high surface area, even hindered fast electron and ion transport in the electrochemical process. How to improve the conduction and mass transfer is still a big challenge for the electrochemical applications of 2D nanomaterials. To solve this issue, this work is focus on the controllable synthesis of 2D nanomaterials and the construction of hierarchical structures based on vertical oriented 2D nanomaterials. The major results were summarized as follow:

In chapter 1, we briefly introduced the structural advantages and research progress of 2D nanomaterials in electrochemical energy storage, catalysis, and adsorption. We summarized the current technology for the synthesis of ultrathin 2D nanomaterials vertically oriented 2D nanomaterials. Based on the related research background, the significance and content of this work were clarified.

In chapter 2, vertically oriented $Mg(OH)_2$ nanosheets were successfully fabricated by controlling the hydrolysis process of MgO. This result opened new opportunities for the design of vertically structured 2D carbon nanomaterials.

In chapter 3, to solve the re-stack problem of 2D ultrathin carbon nanomaterial, vertically oriented ultrathin carbon nanosheets were successfully constructed by using the $Mg(OH)_2$ microrods composed of vertically oriented $Mg(OH)_2$ nanosheets as the templates and dopamine as the carbon precursor. The influence of the organic precursor and calcined temperature on the pore structures of vertically oriented ultrathin carbon nanosheets was studied. When used as anode material for lithium ion batteries, the vertically oriented ultrathin carbon nanosheets showed great advantages in the specific capacity and rate performance. A high reversible specific capacity of 1150 mAh g^{-1} was obtained, which was 3.1 times than that of graphite. Even at a

current density of 10 g^{-1}, a large reversible capacity of 246 mA h g^{-1} was obtained for the as-prepared vertically oriented ultrathin carbon nanosheets.

In chapter 4, to improve the stability and rate performance of lithium sulfur batteries with high sulfur loading, we successfully obtained vertically oriented porous graphene-like nanosheets. With high specific surface area and pore volume of vertically oriented porous graphene-like nanosheets, the corresponding carbon/sulfur composites with high sulfur loading (e.g., 78.9 wt % and 88.8 wt %) exhibited high specific capacities, cyclic properties, and volumetric energy densities. Compared to the 2D and 1D porous carbon structures, vertical oriented graphene porous nanosheets can effectively elevate the rate properties of lithium sulfur batteries as a result of their opened conductive frameworks.

In chapter 5, we developed a MgO strategy for the green and scale-up preparation of ultrathin α-$Ni(OH)_2$ nanosheets at room temperature. Based on the understanding of the formation mechanism, this method can be extended as a general strategy for the synthesis of layered transition metal hydroxides and layered double hydroxides, and their derivatives. Thanks to the high specific surface area, the as-prepared ultrathin α-$Ni(OH)_2$ nanosheets showed excellent performance in the fields of heavy metal adsorption and supercapacitors.

In chapter 6, to solve the re-stacking problem and poor conductivity of 2D transition metal hydroxides, we used the MgO strategy to grow vertically oriented transition metal hydroxide on the targeted substrates at room temperature. Compared with the traditional hydrothermal and electrodeposition methods, the MgO strategy was not subject to the size, shape, and components of substrates. Vertically oriented NiS_2 nanosheets on Ni foam and vertically oriented layered double hydroxide nanosheets (NiFe LDH) with optimized molar ratio of Ni/Fe was synthesized as the catalysts for hydrogen evolution reaction and oxygen evolution reaction, respectively. Based on their enhanced catalytic properties, the vertically oriented NiS_2 and NiFe LDH nanosheets were further used as the cathode and anode for the overall water splitting, respectively. The as-obtained hybrid electrolyzer exhibited a low decomposition voltage of 1.55 V at a current density of 10 mA cm^{-2} in 1 M KOH electrolyte.

Keywords: two-dimensional nanomaterials; vertically oriented structures; energy storage; electrolysis of water; magnesium oxide